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Certificate

Benckiser N.V. of Amsterdam/ the Netherlands filed a patent application entitled

"Composition for use in a dishwasher"

at the German Patent and Trademark Office on 29 July 1998.

The attached documents are a true and exact copy of the original documents pertaining to this patent application.

The application has provisionally been given classification C 11 D 17/00 under the International Patent Classification at the German Patent and Trademark Office.

Munich, 17 August 1999

German Patent and Trademark Office

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New application (Patent)		**BK3642**	28 July 1998

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"Composition for use in a dishwasher"

The present invention relates to a composition for use in a dishwasher and a method of using same.

Although modern dishwashers usually have a plurality of washing programmes which differ in terms of the duration and temperature of the individual washing cycles, all essentially consist of the following basic steps: pre-rinse cycle, main washing cycle; one or more intermediate rinse cycles; a final rinse cycle; and drying. During the course of a dishwasher programme, a series of products is metered into the dishwasher to assist the respective stage of the cycle. For example, whereas the actual dishwasher detergent intended to provide the cleaning action is added at the start of the main washing cycle, special substances are used during the final rinse cycle, e.g. rinse agents. The purpose of rinse agents is to prevent drops

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of water from being left on the rinsed items as they are rinsed with water, which would otherwise leave behind specks of the substances dissolved/dispersed in the drops, in particular salts, after drying.

These two functions, namely the cleaning action of the machine dishwashing agent and the described function of a clear rinsing agent, have until now been brought about using two separate dispensing systems with products that are dispensed at different points during the dishwashing cycle.

In addition to rinse agents, other substances may be used, which become active during the final rinse cycle, e.g. to produce an anti-bacterial action (e.g. cationic compounds or triclosan), protect silver (e.g. benzotriazol), impart fragrance (fragrances, perfume), add bleaching/disinfecting action (e.g. chlorine bleaches), neutralise odours (e.g. polyvinyl pyrrolidone), means of removing deposits and enzymes (e.g. lipase for removing fatty deposits from the washed articles).

The underlying objective of the present invention was to combine the cleaning function and the function(s) of the substance(s) used in the rinse cycle whilst preserving the same performance in terms of results as those which can be achieved by separate dispensing, and to enable substances other than rinsing agent to be dispensed during the rinse cycle.

Patent specifications DE-OS 20 65 153 and DE-OS 20 07 413 disclose detergent tablets for use as washing agents, in which two components with different functions are used in combination with one another. The structure consists of a shell casing, assembled from two shell halves made from a cleansing agent and a cavity enclosed by the shells, containing additives such as softeners, brighteners, etc.

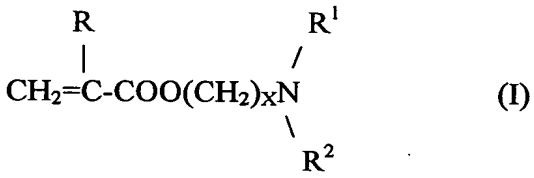
British patent 1 390 503 discloses a liquid cleansing agent or detergent containing capsules, which are insoluble in the composition, but release their contents when the composition is

diluted with water. This objective is achieved by the fact that the capsules are coated with a substance, which is not readily soluble in aqueous solutions with a high ion content but is soluble when the ion content is reduced by dilution. It should be pointed out that this technique can be used as a means of incorporating materials in the liquid detergent which are intrinsically unstable in the liquid detergent or would become unstable if they were added directly. This technique is also suggested as a means of delaying the release of a specific substance. The use of dishwasher rinsing agents is mentioned and the encapsulation of tribromosalicyl anilide is suggested as a means of rendering them stable. The encapsulated material is released within 2 minutes of the detergent being diluted with water, i.e. already during the main washing cycle.

US patent 4,082,678 describes a fabric conditioner, which comprises a closed container enclosing a releasable agent, the purpose of which is to render insoluble in water or non-dispersible in water an inner container, which is normally water-soluble or dispersible in water, disposed inside the first container, the inner container enclosing a fabric conditioner. The inner container consists of a substance whose solubility is largely dependent on the ion concentration or the pH value of the medium and the means used to render the inner container insoluble is a substance for controlling the pH value or ion intensity.

Japanese patent applications KOKAI 60-141705, 61-28440, 61-28441, 61-28596, 61-28597 and 61-28598 describe methods or producing pH-sensitive microcapsules for use in detergents. The pH-sensitive coating is a copolymer of the following monomers:

A) at least one basic monomer of formula (I):



(I)

in which R stands for hydrogen or a methylene group, R^1 and R^2 respectively stand for an alkyl group with 1to3 carbon atoms and x is a whole number from 1 to 4;

B) at least one monomer which is insoluble or not readily soluble in water; and

C) at least one water-soluble monomer.

The described polymers are said to be insoluble at a pH value of 9.5 and higher and soluble at a pH value of 8.5 or less. Cleansing compositions containing different substances are described which can successfully and effectively be coated using the described polymers. The objective of the invention described here is to protect substances which do not release their function until the rinse cycle until the cycle starts and then to delay the release as far as possible. There is no mention of applications involving dishwashers.

A disadvantage of the solution described in these Japanese patent applications is that the encased particles are in direct contact with non-alkaline washing water at the start of the washing cycle which can cause the protective casing to start dissolving.

Japanese patent specification KOKAI 50-77406 discloses a washing detergent, which is encased in a water-soluble casing, obtained by mixing polyvinyl acetal dialkylamino acetate and at least one organic acid, which is solid at room temperature. The purpose of this protective casing is to protect the washing detergent during the main washing cycle and to release it during rinse cycles. The described compound reacts to the change in pH-value between the

main washing cycle and the rinse cycle. Here again, the disadvantage is that the protective casing could start to dissolve at the start of the washing cycle.

European patent applications EP 284 191 A2 and EP 284 334 A2 disclose a water-soluble polymer film for releasing washing additives during the rinse cycle of washing machines, which remain intact during the normal washing cycle over a range of typical temperatures and rapidly dissolve during the rinse cycle. These applications point out that the use of pH-sensitive coatings was admittedly known, but that these films are normally also temperature-sensitive, which means that they can not be relied on to remain stable at the various temperatures of the washing cycle. The proposed solution is a pH-dependent material (which undesirably also has a positive, temperature-dependent dissolving behaviour) combined with a material having a negative, temperature-dependent dissolving behaviour. This combination is supposed to guarantee that the coatings do not dissolve at the high temperatures prevailing at the start of the washing cycle (in particular the very high temperatures used in American machines). There is no mention of applications involving use dishwasher rinsing agents.

European patent application EP 0 481 547 Al discloses multi-layer dishwasher tablets having a core, a separating layer surrounding the core and an outer layer for the sequential release of the substances contained in the different layers. This tablet is basically intended to solve two problems, namely 1) incompatible materials can be formulated together in a single tablet and released at different times in order to avoid mutual interaction and 2) compositions, which are intended to evolve their functions at different times, can be formulated in a single tablet.

A major disadvantage of this prior art is that temperature and in particular the contact time with the washing solution is used as a means of initiating dissolution of the surrounding layer, i.e. the materials used for the material of the cover are sensitive to temperature. Given the fact that temperature/timing in dishwashers can very considerably depending on the selected programme, it is difficult, if not impossible, to find a material that could be used for all the possible programmes which can be run by modern dishwashers. It is in fact admitted in EP 0 481

547 A1 (page 7, lines 37-43) that allowance must be made for the peculiarities of machines and programmes when selecting the material for the covering layer. The practical feasibility of the described products is therefore clearly limited.

PCT application W0 95/29982 discloses a dishwasher rinsing agent in which the release of a clear rinsing agent is delayed, and is provided in the form of a non-ionic surfactant used with an inorganic builder salt forming a core, which is provided with a waxy coating to ensure the delayed release. This coating is a substance which does not melt at the operating temperatures encountered during the cleaning cycle, but which chemically disintegrates so gradually at alkaline pH-values that an effective quantity of clear rinsing agent is still present at the end of the main cleaning cycle and is transferred into the final rinse cycle.

The disadvantage of this is that the coating is rendered soluble by chemical saponification at alkaline pH-values, so that the time at which the clear rinsing substance is released from the core depends on both the temperature and the length of the main cleaning cycle. The patent application contains no teaching as to how a product is to be formulated so that the clear rinsing agent can be released in all washing programmes of any machine type during the clear rinse cycle only. Furthermore, the active substance of the core serving as a rinsing agent is a non-ionic surfactant, which is absorbed on an inorganic builder salt. The rinsing results are therefore not good, in particular leaving marks behind on glass. Finally, the product is a mixture of granular cleaning agents and granular clear rinsing particles.

Against the background of the prior art described above, the underlying objective of the present invention is to propose a composition of the generic type, which can be used for most rinsing programmes of different models of dishwashers and, in each of these cases, the substance(s) which do/does not unleash their action until the rinse cycle are released at the earliest at the start of the rinse cycle. The intention is to achieve this without significantly restricting the selection of substances which can be used as the cleaning agent, the substance(s) used for the rinse cycle and other ingredients of the composition.

This objective is achieved by the invention by means of a composition of the generic type, characterised by a basic composition which starts to function essentially during the main cleaning cycle of the dishwasher; and at least one particle with at least one core containing at least one substance which essentially does not unleash its function until the rinse cycle of the dishwasher, and a covering essentially totally surrounding the core(s) containing at least one compound, the solubility of which increases as the concentration of a specific compound in the surrounding medium decreases; means being provided to prevent the covering from being significantly dissolved or to prevent the covering from being essentially detached from the core (cores) until the start of the rinse cycle.

In one advantageous embodiment, the concentration of the specific compound in the local environment of the particle or particles is high enough until the start of the rinse cycle to prevent the covering of the core or cores from essentially dissolving or becoming detached to any significant degree until that point.

By preference, the particle(s) is/are coated with a substance which becomes detached or separates - essentially irrespective of the concentration of the specific compound in the surrounding medium - during the course of the main washing cycle of the dishwasher.

The basic composition is preferably in the form of a tablet.

In one embodiment proposed by the invention, the at least one particle is placed in or on the tablet in such a way that the concentration of the specific compound in the local environment of the particle or particles is high enough to prevent the coating from being dissolved to any significant degree or detached to any significant degree from the core or cores until the tablet has essentially completely dissolved.

It is particularly preferable if the particle or all the particles is or are accommodated in a cavity of the tablet, totally enclosed by the base composition.

Accordingly, the at least one cavity may contain one or more particles, in which case it alone or all together will essentially occupy the same volume as the cavity.

It is preferable if the at least one cavity has a larger volume than the particle or particles accommodated in the respective cavity.

In an alternative embodiment of the invention, the particle or particles is/are disposed loosely in the cavity.

In another alternative, the particle or particles is/are fixed in the interior of the cavity, preferably by means of an adhesive.

In another embodiment, the cavity is disposed essentially at the centre in the interior of the tablet.

It is also proposed by the invention that the tablet should have a single, substantially spherically shaped cavity.

As proposed by the invention, the cavity accommodates a single, essentially spherically shaped particle, the external diameter of which is smaller than the internal diameter of the cavity.

In another embodiment, the particle or particles is/are accommodated in at least one cavity of the tablet, which is only at least partially surrounded by the base composition.

Accordingly, it is also preferable if the cavity is provided in the form of a depression in one of the surfaces of the tablet, in which the particle or particles is/are only partially received.

In a preferred embodiment, the particle or particles is/are accommodated in the cavity or depression in such a way that it/they does/do not stand proud of (project beyond) the surface(s) of the tablet.

The invention proposes one particular embodiment, in which the cavity or the depression contains only a single particle, the volume and shape of which in the region of the cavity or depression essentially matches the volume and shape of the cavity or depression, which is completely filled by it or them.

The cavity or depression preferably has a substantially spherically shaped cross section parallel with one of the surfaces into which it opens or in which it is disposed.

As proposed by the invention, the cavity or the depression is open at the surface(s) only to the degree that the particle or particles accommodated in it can not pass through the opening(s) of the cavity or depression.

As proposed by the invention, the particle or particles is/are preferably loosely disposed in the cavity or depression.

In an alternative, the particle or particles is/are fixed in the cavity or depression.

In another embodiment of the invention, the particle or particles is/are fixed in the cavity or depression by means of an adhesive.

In a preferred embodiment of the invention, the basic composition contains at least one composition selected from the group consisting of a dishwasher cleaning composition, a water softener composition and a washing intensifier composition.

In a preferred embodiment of the invention, the covering contains at least one compound which is not soluble or is only slightly soluble at the concentration which prevails at the end of the main washing cycle of the dishwasher, but is sufficiently soluble at the concentration of the specific compound prevailing during the rinse cycle for at least some of the material to dissolve or detach from the core(s) so that at least some of the core material is dispensed into the surrounding medium during the rinse cycle.

This being the case, it is preferable if the solubility of the compound increases as the OH ion concentration and hence the pH value in the surrounding medium decreases.

It is particularly preferable if the compound exhibits no or only a low solubility at a pH value above 10, but is sufficiently soluble at a pH value below 9 that it is largely dissolved or detached from the core (cores) during the rinse cycle so that at least some of the core material is dispensed into the surrounding medium during the rinse cycle.

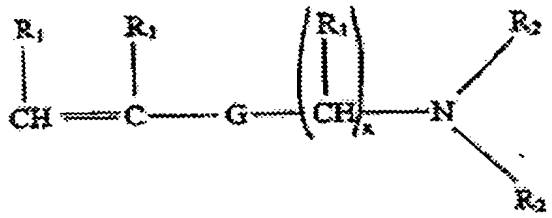
It is also preferable if the compound is a polymer, preferably a pH-sensitive polymer with at least one repeat unit with at least a basic function, which is not part of the backbone chain of the polymer.

In a preferred embodiment, the polymer has at least one repeat unit based on a compound which is selected from the group consisting of vinyl alcohol derivatives, acrylates or alkyl acrylates having said basic function.

The invention also proposes that the polymer should be a carbohydrate which is functionalised with said basic function.

Said basic function is preferably an amine, more especially preferably a secondary or tertiary amine.

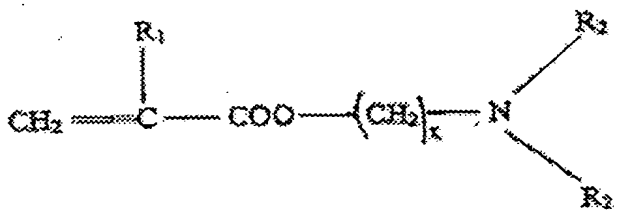
In a preferred alternative, the repeat unit is based on a compound having formula III below:



(III)

in which G is a linking group selected from -COO-, -OCO-, -CONH-, -NHCO-, -NHCONH-, NHCOO-, -OCONH- or -OCOO-, in which R_1, independently of one another, stand for hydrogen or an alkyl group with 1 to 3 carbon atoms, R_2, independently of one another, stand for hydrogen or an alkyl group with 1 to 5 carbon atoms and x is a whole number from 1 to 6.

The repeat unit is preferably a compound having formula IV below:



(IV)

in which R_1, independently of one another, stand for hydrogen or an alkyl group with 1 to 3 carbon atoms, R_2, independently of one another, stand for hydrogen or an alkyl group with 1 to 5 carbon atoms and x is a whole number from 1 to 6.

In another embodiment, the basic function is an imine or a basic aromatic group containing N, preferably a pyridine group or an imidazole group.

In another embodiment, the pH-sensitive polymer is a polymer derived from chitosan.

Finally, it is proposed by the invention that the compound should be k-carrageenan.

In one particular embodiment of the invention, the core (cores) contain(s) at least one material selected from the group consisting of surfactants, anti-bacterial compositions, silver-protecting agents, fragrances, bleaching agents, disinfectants, odour-masking substances, agents for removing deposits and enzymes.

It may be that the core or at least some of the cores are present in the form of encapsulated liquid, preferably in the form of a gelatine capsule containing liquid.

In another embodiment, the core or at least some of the cores are present in solid form.

This being the case, it is preferable if the core or at least some of the cores have a melting point in excess of 35°C, preferably between 55 and 70°C.

The invention further relates to a method of operating a dishwasher cycle in a dishwasher, whereby the composition proposed by the invention is dispensed into the medium contained in the dishwasher at an appropriate point in time during the pre-rinse cycle and the main washing cycle.

In one particular embodiment, if the basic composition in the form of a tablet is not in a position, having dissolved in the medium, to provide a concentration of the specific compound in the medium which is high enough substantially to dissolve the covering and essentially detach

the covering from the core (cores) until the end of the end of the main washing cycle, this sufficient concentration of the specific compound is obtained by adding another composition, such as a dishwasher rinsing composition to the medium of the main cleaning cycle at an appropriate point in time.

The composition proposed by the invention is distinctive due to the fact that it achieves the set objective with outstanding results, both in the main cleaning cycle and during the rinse cycle of a dishwasher. The tablet is dissolved during the main cleaning cycle, so as to provide the intended action (cleaning, water-softening, intensifying the washing effect, etc.). The particle or particles disposed in or on the tablet contain as the core material the substance or substances which are not intended to start their main function until the rinse cycle of the dishwasher, for example rinsing agent.

This (these) substance(s) is/are protected by a covering which is stable at the concentration of a specific compound, e.g. a specific ion such as the OH ion or the H+ ion (and hence a specific pH value) and at the temperature of the main washing cycle and does not dissolve or become detached at all or at least not to any significant degree. Not until the concentration is significantly reduced by dilution, i.e. at the start of the rinse cycle, does the solubility of the covering material become so significantly reduced that it rapidly dissolves or detaches and the actual active core material is released into the surrounding medium. The essential factor is that the core material continues to be protected, due to adding the composition proposed by the invention to the water, until the start of the rinse cycle, i.e. even before the cleaning liquor has reached the point of having a sufficiently high concentration of the specific compound, as will be explained in more detail below.

As an alternative to using the basic compound in the preferred tablet format, it would also be possible to use other dispensing formats and these are also included in the scope of the invention. For example, the particles with the covering which varies in solubility in response to a change in the concentration of the specific compound can be combined with the basic compo-

sition by a granulation or similar process. In order to ensure reduced contact between the covering and basic composition, as may be desirable in this embodiment, the particles can be encased in a further protective casing, e.g. a compound that is soluble in water irrespective of the concentration of the specific compound. With this embodiment, the basic composition and protective casing of the particles dissolve first of all during the main washing cycle, again leaving behind the particles protected with the covering proposed by the invention.

Provided that no special dispensing aids are used for dispensing purposes which might hold back the particles proposed by the invention, the particles proposed by the invention should be large enough to ensure that they are not released to any significant degree on draining after the main washing cycle and the intermediate rinse cycle or intermediate rinse cycles and carried out of the dishwasher.

The invention will now be described in more detail with reference to examples illustrated in the appended drawings. Of the drawings:

Fig. 1 plots the typical pH profile of a dishwasher.

Fig. 2 is a cross section illustrating a first embodiment of the composition proposed by the invention;

Fig. 3 is a cross section illustrating a second embodiment of the composition proposed by the invention;

Fig. 4 is a cross section illustrating a third embodiment of the composition proposed by the invention;

Figs. 5a and 5b are a view in cross section and a plan view illustrating a fourth embodiment of the composition proposed by the invention; and

Fig. 6 is a cross section illustrating a fifth embodiment of the composition proposed by the invention.

The ion concentration profile or pH profile of the washing and rinsing medium in a dishwasher basically depends on the ingredients used for the cleaning composition and rinsing agent., A typical pH profile using a standard basic dishwasher agent, e.g. CALGONIT®, is given in Fig. 1 (dishwasher used: BOSCH model SMS 3047).

The vertically plotted figures indicate the duration of the following steps: pre-rinse, main wash, intermediate rinses, final rinse. It is clear that the pH value during the major part of the main washing cycle is in the range of between 10.0 and 10.5. The pH value falls once the washing liquor is pumped out at the end of the main washing cycle and fresh water is added, reaching a value of 9.0 during the intermediate rinse and a value of between 8.5 and 9.0 during the final rinse cycle.

Figs. 2 to Fig. 6 illustrate possible embodiments of the composition proposed by the invention. In all cases, the preferred format of a tablet is illustrated.

Fig. 2 illustrates a tablet 1, consisting of two half tablets 2 and 3, which may contain a different or the same composition. For example, one of the standard, commercially available 2-layer tablets may be used as the base, in which the two layers are usually of a different composition and differently coloured.

A more or less semi-spherical depression 4 and 5 is provided more or less at the centre of both half tablets, which form a substantially spherical cavity when the tablet 1 is assembled.

In the embodiment illustrated here, a single particle 6 is disposed in this cavity and consists of the core 8 and the covering 9 which is sensitive to pH concentration or ion concentration, the external diameter of which is slightly smaller than the internal diameter of the cavity in the

tablet. In another embodiment of the invention, however, the particle 6 may occupy the cavity completely and will sit against its walls. If the internal diameter of the cavity is slightly larger than the external diameter of the particle 6, the latter can be either loosely placed in the cavity or may be fixed by means of an adhesive placed in the gap.

The advantage gained in the embodiment in which contact between the particle and the base composition is reduced or completely prevented, is that during the manufacturing process, e.g. the consecutive steps of pressing the individual elements, any deformation and potential resultant damage to the core (cores) and/or the covering which would reduce the protective effect of the covering of the core (cores) is reliably prevented. The fact that no pressure is exerted on the particle during any phase of the production process ensures that if specific compositions are used for the core, they will not be able to "bleed" into the material of the covering and basic composition. Finally, for certain compositions of the covering 9 and/or basic composition 2, 3 it may be of advantage to avoid intimate, full-surface contact, since this could otherwise lead to undesirable reactions in the boundary layers.

In a preferred embodiment of the invention, the surface of the particle is at most in partial direct contact with the surface of the basic tablet composition surrounding it. This can be achieved by the means specifically described in this application or by any other means that will achieve the desired objective. Examples of this are arranging a smaller particle loosely in a larger cavity, fixing a smaller particle in the larger cavity such that there is little or only a partial contact between the particle and the basic composition, applying a protective coating to the core covering proposed by the invention, etc.

By the term "local environment" used in conjunction with the particles proposed by the invention is meant the area directly surrounding said particles. The concentration of the specific compound in this local environment of the particle is the factor which determines its stability. In the preferred embodiments in tablet format, this concentration in the local environment of the particle is specifically formulated so that the tablet at least substantially totally dissolves

as the molecules contained in it form a solution. Consequently, the origin of the "specific compound", at least in an initial phase of the main washing cycle, is preferably a compound which is used in the basic composition from which the tablet is made or is generated by it in the surrounding medium. In the most typical case, this will be OH ions (in the case of basic cleaning agents) or H+ ions (in the case of acid lime scale removing agents), the concentration of which, in both cases, can be expressed as the pH-value.

If a (e.g. basic) machine dishwasher composition is not used as the base composition and a water softener composition or wash enhance composition is used instead, for example, it may be that the covering of the particle protected by a sufficiently high concentration of the specific compound in the local environment of the particle can only be guaranteed up to the point at which the basic composition, e.g. the tablet, has totally dissolved, namely in situations where the basic composition is not in a position to provide a sufficiently high corresponding concentration in the washing liquor (and hence in the local environment of the particle or particles) due to the fact that the actual dishwasher detergent (or another special additive) has dissolved.

As a means of fixing the particle in the cavity, it is obviously not only possible to use a conventional adhesive, but also other compositions and means fulfilling the same function, for example mechanical fixing such as an adequate friction contact between tablet and particle, at least at certain points, or a plug connection between tablet and particle. Other fixing agents may also be used between the particle and tablet in the form of compounds which optionally melt or dissolve at the temperature prevailing when water is initially added.

Naturally, a whole range of different geometric shapes may be used for the cavity in the tablet and the particle contained in it, such as ellipsoid, cylindrical, etc., for example. The shape and size of the tablet cavity and of the particle contained in it need not necessarily be the same. Accordingly, a spherical cavity might be used to accommodate a cylindrical particle, for example. All other possible combinations would also be conceivable within the scope of the

present invention. The cavity could also be filled with several smaller particles instead of a single particle.

Fig. 3 illustrates a second embodiment of the composition proposed by the invention, based on a two-layer tablet 1. In this case, the top half-tablet 3 consists of two parts, which provide both an adequate cavity 5 for accommodating the particle 6 and an opening at the side 11 of the tablet. In this case, therefore, the particle 6 is not completely surrounded by the basic composition of the tablet 1 and is visible in the interior of the tablet 1 from outside. Here too, the particle may either be loosely accommodated in the cavity 5 (provided that the size of the particle 6 on the one hand and the size of the opening of the cavity 5 at the side 11 of the tablet on the other are chosen accordingly so that the particle or particles in the cavity are not able to pass through the opening) or can be fixed in the interior of the cavity 5 by appropriate means, such as an adhesive, for example.

Fig. 4 illustrates a third possible embodiment. This one is based on a tablet 1' with a uniform structure, i.e. formed by a single layer 2' of uniform composition and colour. A depression 4' is formed in said layer 2' by means of an appropriate device. The particle 6' is introduced into this depression 4' and in this case is fixed in the depression because the depression is open at the side 11' of the tablet 1' to the degree that the particle would be able to fall out of the depression if it were not fixed and it is therefore fixed by means of an adhesive 10' or by a fixing intermediate layer or by mechanical means (e.g. by friction contact). This same principle may obviously also be used for multi-layer tablets.

Here too, a whole range of different geometric embodiments are possible. .For example, the depression may have a substantially circular cross-section parallel with the side 11'. However, any number of other cross-sections would also be conceivable, e.g. any polygon. As with the embodiment illustrated in Fig. 3, the particle 6' received in the depression 4' may be of any shape (regardless of the shape of the depression 4'), such as an ellipsoid, cylinder, parallelepiped, etc.

It would also be conceivable for the particle 6' to be fixed in a cavity open at both sides, for example in a cylindrical hole 4' extending through the tablet body 1', in which a matching, cylindrical particle 6' is fixed (Figs. 5a and b).

Fig. 6 illustrates another possible embodiment. This is essentially of the same structure as the embodiment illustrated in Fig. 4, i.e. a tablet 1' of uniform construction, i.e. only a single layer 2' of uniform composition and colour. In this instance, instead of a single core (as in Fig. 3), the particle 6" has a number of cores 8", all of which are embedded in a covering 9". In this embodiment it is also possible to incorporate cores of different compositions and different shapes (encapsulated material or solid cores) in one particle 6", for example.

In both the illustrated embodiments and other conceivable alternatives, it is essential that, in order for the particle containing the substance or substances to be released during the clear rinse cycle, there is a local environment, at least during the first phase of the main cleaning cycle, in which there is an adequate concentration of the compound serving as a "trigger" for dissolving the covering, i.e. in a phase in which this concentration is still relatively low, in other words is temporarily within a range in which the solubility of the covering would be increased. This ensures that the covering remains sufficiently stable until the clear rinse cycle.

Example 1

Preparing the core

a. Core for a particle enabling the controlled release of a rinsing agent during the clear rinse cycle

The core of the particle(s) which are not intended to release their action until the clear rinse cycle must contain at least one active substance as a rinsing agent in this specific application. A low-foaming, non-ionic surfactant is advantageously used for this purpose in the present

invention. Such surfactants include, for example, fatty alcohol ethoxylates, fatty alcohol ethoxylate/propoxylates, ethoxylate/propoxylate polymers, such as for example the products of Synperonic® and Brij® range sold by ICI, the products of the Plurafac®, Pluronic® and Lutensol® range sold by BASF, the products from the Genapol® range sold by Clariant and the products of the Polytergent® range sold by Olin.

Other possible examples for such surfactants are alkyl polyglycosides, glucamides and alkyl pyrrolidones. It is obviously possible to use all other surfactants which capable of producing the desired effect as clear rinsing agents.

Most of the known substances used as rinsing agents are liquids or wax-like solids. However, for the purposes of the present invention, the aggregate state of the substance acting as the clear rinsing agent is not of decisive importance. If liquids are used, they can be prepared, prior to applying the covering, in the form of capsules containing surfactant, e.g. gelatine capsules, or can be encased by other appropriate measures. It is standard practice to incorporate solids directly in the covering and the coating process may have to be modified to suit the substance accordingly.

For the purposes of the present invention, molten mixtures have proved to be of particular advantage, resulting in solid surfactant particles with a melting point above 35°C, preferably between approximately 55 and 70°C.

The combinations set out in table 1 detailing different polyethylene glycols with the surfactants Synperonic® RA 30, a block ethylene oxide/propylene oxide, bonded to a C_{13}-C_{15} alcohol (C_{13}/C_{15}-$(EO)_6(PO)_3$) were prepared from molten mixtures in the shape of cylinders weighing approximately 0.25 g. The values found on testing for melting points are given in table 1.

Table 1

Code	RA 30 [%]	PEG 8000 [%]	PEG 10000 [%]	PEG 20000 [%]	PEG 350000 [%]	Melting point [°C]
C1	30		70			58-63
C2	40		60			57-60
A30	50		50			57-60
A31	60		40			54-58
A30	50	50				57-60
C3	60	40				57-60
C4	65	35				55-59
A33	50			50		59-65
C17	60			40		58-63
C18	70			30		57-64
A34	50				50	59-65
C15	60				40	58-66
C16	70				30	57-64

Although all combinations are fundamentally suitable, a 50:50 mixture A33 specifically exhibited excellent stability and was easy to handle, particularly with a view to the subsequent coating process. All samples dissolved rapidly in water, thereby guaranteeing optimum activity as a clear rinsing agent in each case.

The invention is obviously not in any way restricted to the combinations given as examples here. As stated, any surfactant which can be used as a clear rinsing agent may be used for the purposes of the invention.

b. Core for a particle enabling the controlled release of a fragrance in the clear rinse cycle

Dishwasher compositions containing bleaching agents, in other words with an oxidising action, greatly restrict the choice of fragrances which can be used in these compositions. Delaying the release of the fragrance until the clear rinse cycle permits much greater flexibility in the use of fragrances.

In order to control the release of a fragrance or a fragrance composition during the clear rinse cycle, a particle as proposed by the invention can be prepared, for example, from a mixture of 50% by weight of molten polyethylene glycol, e.g. PEG 8000, 25% by weight of fragrance or fragrance composition and 25% by weight of diethyl phthalate, which is cooled to produce a spherical particle weighing 0.75 g, for example.

c. Core for a particle enabling the controlled release of an anti-bacterial composition during the clear rinse cycle

The use of a particle as proposed by the invention with a core or several cores containing the anti-bacterial composition in a tablet formulated for use in a dishwasher opens up the possibility of releasing two different compositions during the clear rinse cycle, namely the anti-bacterial composition from the core(s) of the particle proposed by the invention and the rinsing agent from the usual dispensing system of the dishwasher.

For a particle of this type, a core is prepared from a mixture of 100% of molten benzalkonium chloride (Barquat® MS-100), which is cooled in a mould to produce a spherical particle weighing 0.64 g, for example.

d. Core for a particle enabling the controlled release of enzymes during the clear rinse cycle

Since proteases, which are used as standard in dishwasher compositions, are known to break down lipases and can thus impair their activity, it would be desirable to incorporate such lipases in the core(s) of a particle as proposed by the invention so that the lipases could be controlled and their release delayed until the clear rinse cycle, which would enable the enzymes to work to their full effect.

To this end, for example, 0.4 g of a granular lipolytic enzyme (e.g. Lipotase® 100T (Novo)) is used, contained in a hard gelatine capsule of a rounded cylindrical shape, for example, of the type such as used for drugs.

Example 2

Screening process for covering materials

As mentioned above, it is of crucial importance to the present invention that the material used for the covering of the particle core or cores containing the substance or substances which essentially do not start their function until the clear rinse cycle of the dishwasher has a solubility which is dependent on the concentration of a specifically selected compound. Accordingly, the covering containing a compound whose concentration is specifically formulated is essentially insoluble during the main washing cycle but is rendered soluble and becomes detached from the particle as this concentration drops during the intermediate rinse cycle or cycles.

It has been found that the dilution which results when the washing liquor is pumped out and fresh water introduced reduces the concentration by 20 to 200 times during the course of the various rinsing cycles between the end of the main washing cycle and the final rinse cycle.

On the basis of this observation, processes have been developed for screening different polymers for their suitability for use in such covering or casing materials, which involve determining the solubility of such polymers at two different concentrations, differing from one another by a factor of at least 20 and preferably 200.

The concentration values to be used during polymer screening depend on the formulation of the basic composition of the tablet in which the encased or covered particle is to be incorporated.

The value of the highest concentration used for the screening process will actually depend on the concentration of the selected compound encountered in the washing liquor and the dishwasher detergent has completely dissolved. Once this concentration has been determined, the lower values for the concentration should be fixed at 20 to 200 times below this higher value.

On the basis of this information, it will be within the routine capacity and knowledge of a person skilled in this field to determine the concentration values for the test solutions to be used in the testing processes described below.

Method of preparing the test solution and conducting and evaluating the test

The materials to be tested are dissolved in solvents in which they are readily soluble. The solutions are placed on glass plates and then dried at room temperature until they exhibit a constant weight.

The glass plates are placed in a beaker with the test solution at a controlled temperature. The solution is then stirred with a magnetic stirrer at a controlled stirring rate. After about 10 minutes, the glass plates are removed from the beaker and dried at room temperature to a constant weight. The results are expressed as a (%) weight loss.

Naturally, the screening processes must be adapted to suit the basic composition because it is this which essentially influences the concentration of the specific compound, e.g. the pH-profile, in the dishwasher cycle. The objective in all cases is to check the degree of solubility of the corresponding materials in different states, namely at high or low concentration of the specific compound or pH-values.

Having obtained this information, it is within the routine capacity of a person skilled in this field to determine the specific test parameters for screening purposes. Two examples of screening processes are described below, which were used to test some of the materials which might be potentially used as materials for the covering of the particle proposed by the invention.

Screening process 1

Screening process 1 was conducted using buffer solutions as a medium for simulating the washing liquor. Two buffer solutions were used for this purpose, prepared in the following manner:

Stock solution:	7.507 glycine buffer (Merck 104169) 5.850 g NaC1 topped up with water to 1000 ml
pH 8 buffer solution:	500 ml stock solution 500 ml distilled H_20 1.23 g 1 N NaOH
pH 10-buffer solution:	500 ml stock solution 500 ml distilled H_20 32.6 g 1 N NaOH.

Screening process 2

Screening process 2 was conducted using the following detergent formulations in order to simulate corresponding conditions during different stages of the dishwasher cycle. Concentrations of 4 to 5 g/l are standard for the quantity of detergent dispensed during the washing cycle. Concentrations of approximately 20-40 mg/l are standard for the clear rinse cycle.

Detergent formulation:

Substance	% by weight
Sodium perborate monohydrate	9.00
Sodium polyphosphate	48.00
Sodium carbonate	28.00
Polyethylene glycol	4.00
Polymer	1.50
TAED	3.00
Enzymes	1.50
Surfactant	3.50
Additives	1.50
Total	100.00

Screening process 3

Screening process 3 is used for screening compounds, the solubility of which changes depending on the concentration of potassium ions. The compounds found using this screening method can be used if - as explained above - a correspondingly high concentration of potassium ions is present during the main washing cycle, which is reduced accordingly by dilution during the clear rinse cycle.

Screening process 3 was conducted using the formulation below as a means of simulating the relevant conditions.

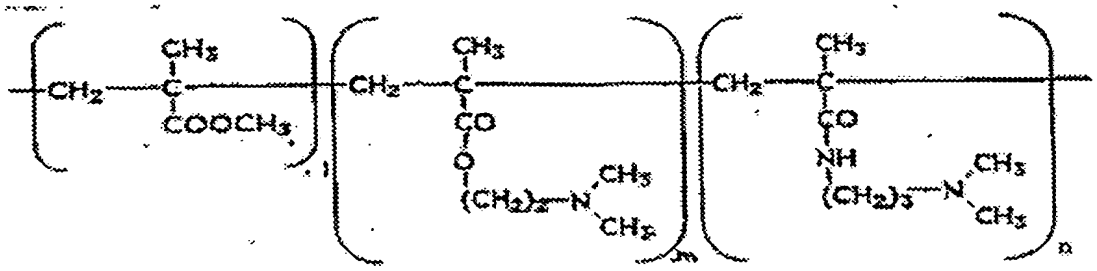
Formulation:

Ingredient	% weight
Potassium phosphate	13.6
Potassium bicarbonate	34.00
Potassium sulphate	23.1
Potassium chloride	12.4
Potassium carbonate	9.7
Boric acid	2.0
Sodium perborate monohydrate	2.0
TAED	1.0
Paraffin	1.0
Protease	0.2

Example 3

Selecting materials for covering the particles

Using the screening process described in example 2, different materials were tested for their suitability as a covering for the particles proposed by the present invention. One of these materials, hereafter referred to as "polymer 1", is a polymer as described in Japanese patent application KOKAI 61-28440, i.e.. a polymer of general formula II in which $1/(1+m+n) = 0.35$; $m/(l+m+n) = 0.45$; $l+m+n = 1500\text{-}1800$.



(II)

The polymer was produced in the usual manner by bulk polymerisation. The results of screening test 1A were as follows:

Screening test 1:

Films of polymer 1 were made from a 10%-strength solution in isopropanol.

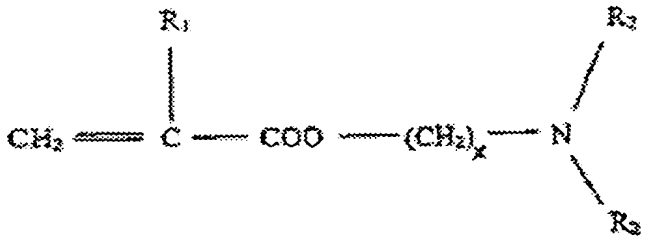
pH value of the buffer solution	Weight loss at 25°C [%]	Weight loss at 65°C [%]
10	7-8	5-8
8	81-88	91-95

Screening process 2:

Films of polymer were made up from a 10%-strength solution of water and 1 N HCl (17:1).

Concentration of detergent pH value	Weight loss at 25°C [%]	Weight loss at 65°C [%]
4 g/l 10.6	8-15	6-16
0.02 g/l 8.5	90-95	89-95

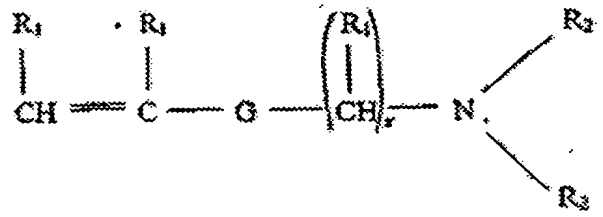
The invention is naturally not restricted to this example of a polymer and there is clearly already considerable scope for potential variations in terms of the polymers specified in Japanese patent applications KOKAI 60-141705, 61-28440, 61-28441, 61-28596, 61-28597 and 61-28598 and as regards extending the range of compounds based on formula IV:



(IV)

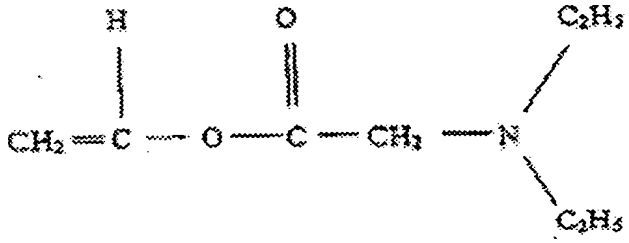
in which R_1 independently of one another stand for hydrogen or an alkyl group with 1 to 3 carbon atoms, R_2 independently of one another stand for hydrogen or an alkyl group with 1 to 5 carbon atoms and x is an whole number integer from 1 to 6.

It would also be possible to use polymers with a repeat unit from the broader category of compounds of formula III:



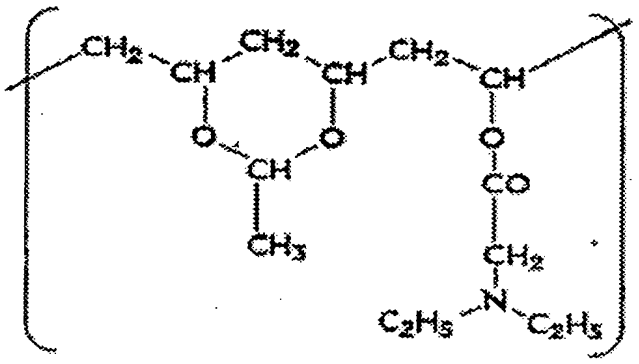
(III)

in which G is a link group selected from -COO-, -COC-, -CONH-, -NHCO-, -NHCONH-, -NHCOO-, -OCONH- or -OCOO-, R_1 independently of one another stand for hydrogen or an alkyl group with 1 - 3, R_2 independently of one another stand for hydrogen or an alkyl group with 1-5 carbon atoms, and x is a whole number from 1 to 6, based on a composition of formula V



(V)

for example a pH-sensitive polymer ("polymer 2") with the repeat unit VI, which is commercially available from the SANKYO company under the registered trade name AEA®,



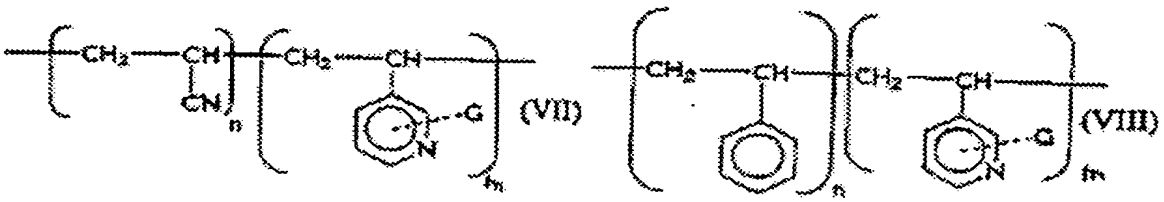
(VI)

Screening process 2 described above was also conducted using "polymer 2".

15 g of "polymer 2" and 5 g of Mowiol® 3-98 (Clariant) were dissolved in a mixture of water/ ethanol/ 1N HCl 12:8:1. Films were formed and tested in the manner described above. The results are set out below:

Concentration of detergent pH value	Weight loss at 25°C [%]	Weight loss at 65°C [%]
4 g/l 10.6	2-8	5-7
0.02 g/l 8.5	32-40	45-47

Other polymers which have the desired characteristics or which can be easily modified to render them suitable for the purposes of the present invention, are polymers of isomers or derivatives of pyridine, preferably copolymers with styrene or acrylonitrile, having formulas VII and VIII below, in which G is a substituent at any point on the pyridine ring.

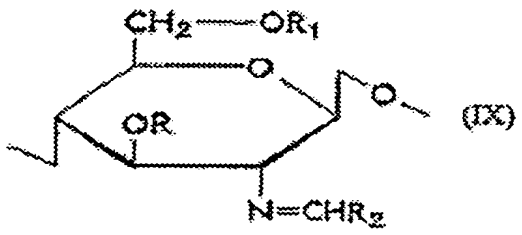


A polymer of formula VIII above, namely poly(4-vinylpyridine-styrene) copolymer (Scientific Polymer Products, Inc.) "polymer 3", was tested using screening process 2 described above:

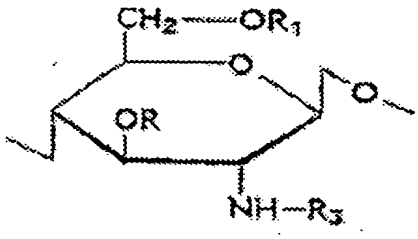
10 g of "polymer 3" were dissolved in 230 ml of water/ 1N HCl 6.25:1. Films were formed and the tests conducted as described above. The results are set out below:

Concentration of detergent pH value	Weight loss at 25°C [%]	Weight loss at 65°C [%]
4 g/l 10.6	0-6	5-12
0.02 g/l 8.5	68-85	92-94

Other polymers are (e.g. statistical) polymers derived from chitosan, based on the following monomer units IX and X



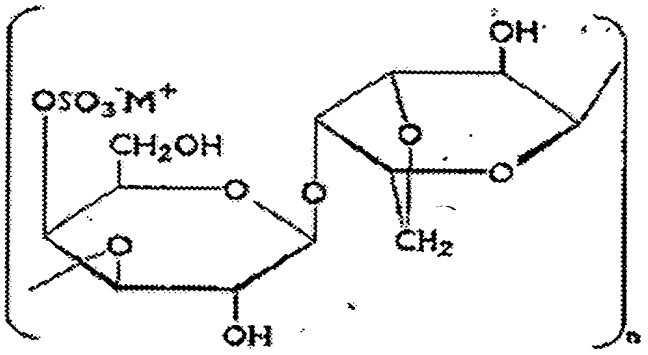
(IX)



(X)

It would also be possible to use substances or mixtures of substances in the covering for the core material which, in terms of their solubility behaviour, react to a change in ion concentration, i.e. polymers sensitive to ion concentration. The partially hydrolysed polyvinyl acetates disclosed in patent specifications EP 0 284 191 A1 and EP 0 284 334 A2 may be considered for this purpose and are commercially available under the registered trade name Mowiol® (Clariant), which exhibit an appropriate dependence on ion concentration due to complexing of the borates with polyols. Initial tests have been successfully conducted with Mowiol® 56-88.

Another polymer that is sensitive to ion concentration is polysaccharide k-carrageenan, which was tested by screening process 3 (see example 2), which showed it to be a polymer whose solubility is dependent on the concentration of potassium ions in the surrounding medium. K-carrageenan is represented by formula XI below:



(XI)

This polymer, which will be referred to as "polymer 4", was tested using screening process 3 described above.

4 g of k-carrageenan were dissolved in 96 g of water. 10 g of Mowiol® 18-88 were dissolved in 90 g of water and the two solutions mixed. The resultant solution was used to form the films and run the test, as described above. The results are set out below.

Concentration of cleansing agent	Weight loss at 30°C [%]	Weight loss at 60°C [%]
4 g/l	0.5-3.0	11.0-12.0
0.02 g/l	24.5-25.0	78.0-85.0

The above list of compounds suitable for the covering proposed by the invention is naturally not exhaustive. Other polymers with a solubility which changes when the concentration of a specific compound is varied, e.g. the pH value, within the desired range could conceivably be used or could be developed and are therefore also included within the scope of the present invention. Other compounds which might be considered for use as a covering proposed by the invention are those with a solubility which reacts to changes in the concentration of non-ionic compounds in the surrounding medium. Furthermore, the substances which are suitable for

use in the covering proposed by the invention are not restricted to polymeric compounds, although these are the substances described here as the preferred embodiments.

The screening processes described above or other screening methods suitable for measuring sensitivity to a concentration may be used to test other different materials, either commercially available or which can be obtained by simple modifications, for their suitability for use with the present invention. The average person skilled in this field would have no difficulty selecting these polymers by specifying an objective and applying the screening process with a view to meeting this objective accordingly.

Example 4

Preparing a particle as proposed by the invention

The different cores described in example 1 were used as a basis for manufacturing particles as proposed by the invention. These cores, individually or severally (Fig. 6), were provided with a covering by placing them in a device used to apply a film coating, of the type commonly used in the pharmaceutical industry (for example sold by the Lödige, Hüttlin, GS, Manesty and Driam companies).

In situations where the core(s) contain(s) a substance which exhibits a certain incompatibility with the material of the covering, the core can be provided with a protective coating prior to applying the covering. Various materials known from the prior art may be used for this purpose, such as cellulose, cellulose derivatives, polyvinyl alcohol, polyvinyl alcohol derivatives and mixtures thereof. If using the cores described in example 1, the protective coating used for 1a may be one which preferably contains a 10 % by weight aqueous solution of polyvinyl alcohol, respectively the polyvinyl alcohol Mowiol® 5-88 (Clariant). The quantity of coating applied may easily be varied by the skilled person depending on the composition of the core or cores and adjusted accordingly. Good results have been obtained from initial tests using the

polymer in a quantity (dry weight) of 3 % by weight in the case of 1a, 2 % by weight in the case of 1b, 3 % by weight in the case of 1c and 4 % by weight in the case of 1d.

The concentration-sensitive covering may essentially be applied to the core or cores or on top of the protective coating in any quantity and thickness, provided care is taken to ensure that the covering will dissolve or detach sufficiently well during the clear rinse cycle that the substance contained in the core or cores is able to unleash its effect. In a preferred embodiment, the concentration-sensitive covering material is applied to the core in a quantity (dry weight) of 1 - 10 % by weight, preferably 4 - 8 % by weight, by reference to the weight of the particle as a whole.

The size of the particles proposed by the invention is preferably such that they are not carried out of the dishwasher during the draining process after the main washing cycle and the intermediate rinse cycle or least not to any significant degree. To this end, a size of approximately 1 cm diameter is usually sufficient. Smaller or larger dimensions may naturally also be selected, provided the overall function can still be guaranteed.

In other tests, "polymer 1" from example 3 was used for the covering and applied as a 10%-strength solution of the polymer in 0.555 N of aqueous HCl.

Example 5

Preparation of 2-layer dishwasher tablets with a clear rinse particle

A typical 2-layer dishwasher tablet suitable for accommodating a particle or rinsing agent in a cavity, as proposed by the invention, can be made by compressing the powdered ingredients in machines that are essentially known from the prior art using standard operating parameters. One possible format for such a tablet is a square-shaped tablet comprising two layers essentially of identical thickness, the largest surface of these layers incorporating a semi-spherical

depression so that the two halves form a substantially spherical cavity in the interior when the two half-tablets are assembled (see Fig.2).

The composition of the tablet is set out in Table 2 below. Other compositions may naturally also be considered, particularly those which are optimised for supporting the compound surrounding the core - for example in terms of generating alkalinity.

Table 2

	White layer	Coloured layer
	50 %	50 %
Sodium perborate monohydrate	18.00	
Sodium tripolyphosphate	48.00	48.00
Sodium carbonate	24.00	32.00
Polyethylene glycol 6000	3.00	5.00
Polymer		3.00
TAED		6.00
Enzymes		3.00
Colouring agent		0.02
Surfactant	4.50	2.50
Additives	2.50	0.50
	100.00	100.00

For the tests conducted in examples 6 and 7, half-tablets weighing approximately 11.5 g were made up. The cavity formed when the two half-tablets are assembled has an internal diameter of approximately 1.2 cm.

The rinse agent particle made as described in examples 1a and 4 is introduced into the semi-spherical depression in the white or coloured half-tablet. A fixing substance such as an adhesive (e.g. polyethylene glycol, polyvinyl ether, polyvinyl alcohol, silicate, preferably molten PEG 4000) is then applied to the corresponding surface of the half-tablet and optionally also the rinse agent particle, and the second half-tablet (coloured or white) is pressed onto the first half-tablet incorporating the rinse agent particle.

Example 6

In this example, a test is described which provides evidence of the coating of the rinse agent-surfactant during the clear rinse cycle using a tablet made as described in example 5.

The rinse agent particles contain surfactant and polyethylene glycol in a mean quantity of approximately 0.37 g respectively. The mean quantity of water during the clear rinse cycle is approximately 5.0 l. The maximum quantity of surfactant plus PEG which can be expected in the clear rinse cycle using one tablet per dishwasher cycle should therefore be 0.148 g/l.

Three different tests were conducted with three different tablets in a BOSCH SMS 3047 dishwasher. The water hardness was approximately 17° dH.

1. Dishwasher tablet without rinse agent particle; temperature 65°C.

2. Dishwasher tablet with rinse agent particle (example 6); temperature 65°C.

3. Dishwasher tablet with rinse agent particle (example 6); temperature 55°C.

In each test a minimum of 1 litre of washing liquor was removed from the clear rinse cycle shortly before the water was drained. The samples were labelled 1.1 to 3.3. The liquor was

then analysed in order to determine the total quantity of surfactant plus polyethylene glycol in the clear rinse cycle. The measurements were performed by extracting the surfactant and PEG, evaporating the solvent and using gravimetric means to measure the non-volatile residue.

It should be pointed out that this analytical method enables both the non-ionic surfactant and the polyethylene glycol to be measured.

	Test 1 mg/l	(n=1) %	Test 2 mg/l	(n=2) %	test 3 mg/l	(n=3) %
n.1	1.0		43.6	29.5	91.9	62.1
n.2	10.4		48.8	33.0	64.2	43.4
n.3	7.0		32.7	22.1	76.5	51.7

Example 7

The test described in this example is used for testing the composition proposed by the invention for effectiveness in the clear rinse cycle.

As a comparison with the dishwasher tablet proposed by the invention incorporating clear rinsing agent particles, as produced in example 6, the rinsing efficiency of a separately added dishwasher agent and clear rinsing agent was tested. The dishwasher agent corresponded to the composition of the tablet proposed by the invention and a commercial clear rinsing agent was used. A BOSCH SMS 3047 dishwasher was used. The water hardness was approximately 17 to 19° dH. The temperature was 65°C. The dishwasher was loaded with 20 glasses, 20 black porcelain plates and 20 items of cutlery.

The dishwasher load was soiled as follows:

50 g of minced meat (pork : beef 1:1) were roasted with 2 g of fat. Once the meat had turned a slightly brownish colour, gravy was added containing 100 ml of water, 1 g of sauce thickener and 2.5 g of instant gravy.

This material was loaded in the dishwasher and the screen was closed with a plug in order to leave the dirt in the machine until the end of the washing programme. The dishwasher agent was introduced at the start of the clear rinse cycle. The dishwasher load was evaluated 10 minutes after the end of the rinse cycle.

A visual evaluation was conducted on the following basis:

4 points = no marks
3 points = 1 to 4 marks
2 points = more than 4 marks up to 1/4 of the surface spotted with marks
1 point = 1/4 to 1/2 of the surface spotted with marks
0 points = almost completely covered with marks.

Effectiveness in preventing marks or spots is expressed as a percentage, 100% efficiency representing the maximum number of 228 points. The results are set out in table 4.

Table 4

Effectiveness			
	Detergent + 2ml rinse agent	Detergent + 2 ml rinse agent	Tablet with rinse agent particle
Porcelain	66.9	75.6	96.9
Glass	25.6	26.9	49.4
Cutlery	80.6	90.6	78.8
Total	57.7	64.4	75.0

The results reveal an excellent performance for the rinsing agent incorporating the composition proposed by the invention. This was particularly evident in the case of porcelain and glass, the efficiency in the case of cutlery being comparable with that of conventional compositions. Surprisingly, the rinsing efficiency of the composition proposed by the invention was even superior to the conventional procedure of adding dishwashing agent and rinsing agent separately in some cases.

The characterising features of the invention disclosed in the description, claims and drawings may essentially be used individually and in any combination to implement the different embodiments of the invention.

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Patent application (Patent)		**BK3669**	28 July 1998

Benckiser N.V., WTC AA Schiphol Boulevard 229, 1118 BH Schiphol Airport Amsterdam, Netherlands
"Composition for use in a water reservoir "

Claims

1. Composition for use in a dishwasher characterised by

   - a basic composition (2, 3; 2') which starts to function essentially during the main cleaning cycle of the dishwasher; and

   - at least one particle (6; 6'; 6") with

   - at least one core (8; 8'; 8") containing at least one substance, which does not unleash its function until the rinse cycle of the dishwasher; and

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- a covering (9; 9'; 9") essentially totally surrounding the core or cores and containing at least one compound, the solubility of which increases as the concentration of a specific compound in the surrounding medium decreases;

means being provided so that the covering (9; 9'; 9") of the core (8; 8') or cores (8") is essentially prevented from significantly dissolving or becoming substantially detached until the start of the rinse cycle.

2. Composition as claimed in claim 1, characterised in that the concentration of the specific compound in the local environment of the particle or particles (6; 6'; 6") is high enough until the start of the rinse cycle to prevent the covering (9; 9'; 9") of the core (8; 8') or cores (8") from essentially dissolving or to prevent the covering (9; 9'; 9") from becoming detached to any significant degree until that point.

3. Composition as claimed in claim 2, characterised in that the particle(s) (6; 6'; 6") is/are coated with a substance which becomes detached or separates - essentially irrespective of the concentration of the specific compound in the surrounding medium - during the course of the main washing cycle of the dishwasher.

4. Composition as claimed in one of claims 1 to 3, characterised in that the basic composition is in the form of a tablet (1; 1').

5. Composition as claimed in claim 4, characterised in that at least one particle (6; 6'; 6") is placed in or on the tablet (1; 1') in such a way that the concentration of the specific compound in the local area around the particle or particles is high enough to prevent the covering from being dissolved to any significant degree or detached to any significant degree from the core or cores until the tablet (1; 1') has essentially completely dissolved.

6. Composition as claimed in claim 5, characterised in that the particle or all the particles (6) is or are accommodated in a cavity (4, 5) of the tablet (1), totally enclosed by the base composition (2, 3).

7. Composition as claimed in claim 6, characterised in that the at least one cavity (4, 5) may contain one or more particles (6), in which case it alone or all together will essentially occupy the same volume as the cavity (4, 5).

8. Composition as claimed in claim 6, characterised in that the at least one cavity has a larger volume than the particle or particles (6) accommodated in the respective cavity (4, 5).

9. Composition as claimed in claim 8, characterised in that the particle or particles (6) is/are disposed loosely (4, 5) in the cavity.

10. Composition as claimed in claim 8, characterised in that the particle or particles (6) is/are fixed in the interior of the cavity (4, 5).

11. Composition as claimed in claim 10, characterised in that the particle or particles (6) is/ are fixed in the interior of the cavity (4, 5) by means of an adhesive.

12. Composition as claimed in claim 10, characterised in that the cavity (4, 5) is disposed essentially at the centre in the interior of the tablet (1).

13. Composition as claimed in one of claims 6 to 12, characterised in that the tablet (1) has a single, substantially spherically shaped cavity (4, 5).

14. Composition as claimed in one of claims 8 to 13, characterised in that the cavity (4, 5) accommodates a single, essentially spherically shaped particle (6), the external diameter of which is smaller than the internal diameter of the cavity.

15. Composition as claimed in claim 5, characterised in that the particle or particles (6'; 6") is/are accommodated in at least one cavity (4') of the tablet (1'), which is only at least partially surrounded by the base composition (2').

16. Composition as claimed in claim 15, characterised in that the cavity is a depression (4') in one of the surfaces (11') of the tablet (1'), in which the particle or particles (6'; 6") is/are at least partially received.

17. Composition as claimed in claim 15 or 16, characterised in that the particle or particles (6'; 6") is/are accommodated in the cavity or depression (4') in such a way that it/they do/does not stand proud of (project beyond) the surface(s) (11') of the tablet (1').

18. Composition as claimed in claim 15 to 17, characterised in that the cavity or the depression (4') contains only a single particle (6'; 6") , the volume and shape of which in the region of the cavity or depression essentially matches the volume and shape of the cavity or depression (4') and essentially completely fills it or them.

19. Composition as claimed in one of claims 15 to 18, characterised in that the cavity or depression (4') has a substantially spherically shaped cross section parallel with one of the surfaces (11') into which it opens or in which it is disposed.

20. Composition as claimed in one of claims 15 to 19, characterised in that the cavity or the depression (4') is open at the surface(s) (11) only to the degree that the particle or particles (6'; 6") accommodated in it can not pass through the opening(s) of the cavity or depression (4').

21. Composition as claimed in claim 20, characterised in that the particle or particles (6'; 6") is/are preferably loosely disposed in the cavity or depression (4').

22. Composition as claimed in one of claims 15 to 20, characterised in that the particle or particles (6'; 6") is/are fixed in the cavity or depression (4').

23. Composition as claimed in claim 22, characterised in that the particle or particles (6'; 6") is/are fixed in the cavity or depression (4') by means of an adhesive (10').

24. Composition as claimed in one of the preceding claims, characterised in that the basic composition (2; 3'; 2) contains at least one compound selected from the group consisting of a dishwasher cleaning composition, a water softener composition and a washing intensifier composition.

25. Composition as claimed in one of the preceding claims, characterised in that the covering (9; 9'; 9") contains at least one compound which is not soluble or is only slightly soluble at the concentration of the specific compound which prevails at the end of the main washing cycle of the dishwasher, but is sufficiently soluble at the concentration of the specific compound prevailing during the rinse cycle for at least some of the material to dissolve or detach from the core(s) so that at least some of the core material is dispensed into the surrounding medium.

26. Composition as claimed in claim 25, characterised in that the solubility of the compound increases as the OH ion concentration and hence the pH value in the surrounding medium decreases.

27. Composition as claimed in claim 26, characterised in that compound exhibits no or only a low solubility at a pH value above 10, but is sufficiently soluble at a pH value below 9 that it is largely dissolved or detached from the core (cores) during the rinse

cycle so that at least some of the core material is dispensed into the surrounding medium during the rinse cycle

28. Composition as claimed in one of claims 25 to 27, characterised in that the compound is a polymer.

29. Composition as claimed in claim 28, characterised in that the compound is a pH-sensitive polymer with at least one repeat unit with at least a basic function, which is not part of the backbone chain of the polymer.

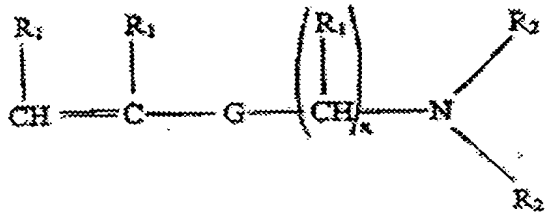
30. Composition as claimed in claim 29, characterised in that the polymer has at least one repeat unit based on a compound which is selected from the group consisting of vinyl alcohol derivatives, acrylates or alkyl acrylates having said basic function.

31. Composition as claimed in claim 29, characterised in that the polymer is a carbohydrate which is functionalised with said basic function.

32. Composition as claimed in one of claims 29 to 31, characterised in that the basic function is preferably an amine.

33. Composition as claimed in claim 32, characterised in that the basic function is a secondary or tertiary amine.

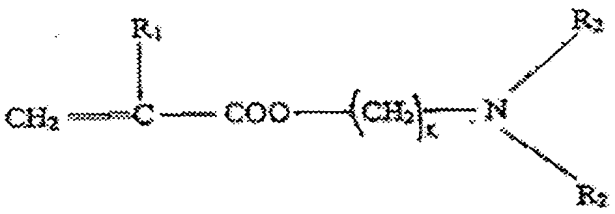
34. Composition as claimed in claim 33, characterised in that the repeat unit is based on a compound having formula III below:



(III)

in which G is a linking group selected from -COO-, -OCO-, -CONH-, -NHCO-, -NHCONH-, NHCOO-, -OCONH- or -OCOO-, in which R_1, independently of one another, stand for hydrogen or an alkyl group with 1 to 3 carbon atoms, R_2, independently of one another, stands for hydrogen or an alkyl group with 1 to 5 carbon atoms and x is a whole number from 1 to 6.

35. Composition as claimed in claim 34, characterised in that the repeat unit is a compound having formula IV below:



(IV)

in which R_1, independently of one another, stand for hydrogen or an alkyl group with 1 to 3 carbon atoms, R_2, independently of one another, stand for hydrogen or an alkyl group with 1 to 5 carbon atoms and x is a whole number from 1 to 6.

36. Composition as claimed in one of claims 29 to 31, characterised in that the basic function is an imine.

37. Composition as claimed in one of claims 29 to 31, characterised in that the basic function is a basic aromatic group containing N.

38. Composition as claimed in claim 37, characterised in that the basic function is a pyridine group.

39. Composition as claimed in claim 37, characterised in that the basic function is an imidazole group.

40. Composition as claimed in claim 31, characterised in that the pH-sensitive polymer is a polymer derived from chitosan.

41. Composition as claimed in claim 25, characterised in that the compound is k-carrageenan.

42. Composition as claimed in one of the preceding claims, characterised in that the core (cores) contain(s) at least one material selected from the group consisting of surfactants, anti-bacterial compositions, silver-protecting agents, fragrances, bleaching agents, disinfectants, odour-masking substances, agents for removing deposits and enzymes.

43. Composition as claimed in claim 42, characterised in that the core (8; 8') or at least some of the cores (8") are present in the form of encapsulated liquid.

44. Composition as claimed in claim 43, characterised in that the core (8; 8') or at least some of the cores (8") are present in the form of a gelatine capsule containing liquid.

43. Composition as claimed in claim 42, characterised in that the core (8; 8') or at least some of the cores (8") are present in solid form.

46. Composition as claimed in claim 45, characterised in that the core (8; 8') or at least some of the cores (8") have a melting point in excess of 35°C.

47. Composition as claimed in claim 46, characterised in that the core (8; 8') or at least some of the cores (8") have a melting point of between 55 and 70°C.

48. Method of operating a dishwashing cycle in a dishwasher, whereby a composition as claimed in one of claims 1 to 47 is dispensed into the medium contained in the dishwasher at an appropriate point in time during the pre-rinse cycle and the main washing cycle.

49. Method as claimed in claim 48, characterised in that, if the basic composition in the form of a tablet is not in a position, having dissolved in the medium, to provide a concentration of the specific compound in the medium which is high enough substantially to dissolve the covering and essentially detach the covering from the core (cores) until the end of the end of the main washing cycle, this sufficient concentration of the specific compound is obtained by adding another composition, such as a dishwasher rinsing composition to the medium of the main cleaning cycle at an appropriate point in time.

Abstract

Composition for use in a dishwasher, characterised by a basic composition which starts to function essentially during the main cleaning cycle of the dishwasher; and at least one particle with at least one core containing at least one substance which essentially does not unleash its function until the rinse cycle of the dishwasher, and a covering essentially totally surrounding the core(s) containing at least one compound, the solubility of which increases as the concentration of a specific compound in the surrounding medium decreases; means being provided to prevent the covering from being significantly dissolved or to prevent the covering from being essentially detached from the core (cores) until the start of the rinse cycle, as well as a method of operating a dishwashing cycle in a dishwasher using the composition proposed by the invention.